

SPECTROPHOTOMETRIC STUDY ON  
CHELATES OF TRANSITION METALS WITH  
NICOTINYLDIHYDROXYAMIC ACID, CINNAMOHYDROXYAMIC  
AND POTASSIUM 2-FUROHYDROXYAMATE

by

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## INTRODUCTION AND LITERATURE REVIEW

Hydroxamic acids have received considerable attention in the last two decades as analytical reagents. Many transition metal ions chelate with hydroxamic acids to form soluble, colored species or insoluble precipitates. Thus, both colorimetric and gravimetric schemes have been developed for quantitative determinations involving metal ions and hydroxamic acids.

Hydroxamic acids may be regarded as derivatives of hydroxylamine ( $\text{NH}_2\text{OH}$ ) with either one or both of the hydrogens on nitrogen being replaced by organic groups. Monohydroxamic acids have the structure



and may be either alkyl or aryl substituted.



or



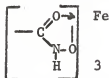
They are weak acids having ionization constants in the range of  $n \times 10^{-8}$  to  $n \times 10^{-10}$  (11). All monohydroxamic acids react with ferric chloride to give a characteristic violet color. As compounds of the type  $\text{RCONHOR'}$  or  $\text{RC(OH)=NOR'}$  do not give a violet color with ferric chloride and structures such as



and

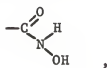


do<sup>(27)</sup>, the structure accepted for this colored species is

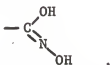


Thus, monohydroxamic acids are bidentate chelating agents which form 5-membered rings.

As well as existing in the hydroxyamide form,

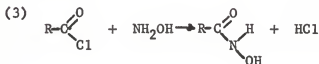
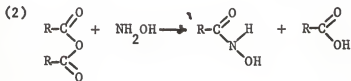
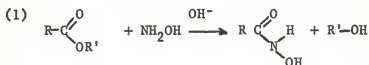


the tautomeric hydroxyoxime form,



has been shown to exist<sup>(13)</sup>. The latter form is less stable, however, and upon standing the hydroxamic acid is converted to the more stable hydroxamic acid form.

Monohydroxamic acids can be prepared by the action of hydroxylamine on the appropriate ester, acid anhydride, or acid chloride<sup>(15)</sup>.

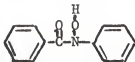


They are most commonly prepared from the ester.

The above reactions have been exploited in a qualitative test for the determination of ester, acid chloride, or acid anhydride groups<sup>(23)</sup>. An ester, acid anhydride, or acid chloride group will give an intense violet color when hydroxylamine hydrochloride and ferric chloride are added to it.

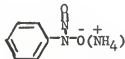
This has been extended to a quantitative study by Goddu, Le Blanc, and Wright<sup>(11)</sup>. Spectrophotometric measurements were made of the intensity of the red-violet iron (III) hydroxamates and from this, esters and anhydrides could be determined quantitatively.

Gravimetric determinations of metal ions involving hydroxamic acids are especially effective with N-aryl substituted hydroxamic acids such as N-benzoylphenyl hydroxylamine. This compound has the structure



which differs from the analytical reagent, cupferron, only slightly.

Cupferron has the structure



N-substituted hydroxamic acids have a higher molecular weight and are more insoluble in aqueous solution than those acids which are not N-substituted. Thus, they lend themselves well to gravimetric precipitations of transition metal ions.

N-Benzoylphenylhydroxylamine has been employed to gravimetrically determine gallium as  $\text{Ga}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_3$  from acidic solution<sup>(1)</sup>, and titanium as  $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})$ <sup>(14)</sup>, from hot acid solution.

Niobium and tantalum have been quantitatively recovered by precipitation with N-cinnamoylphenylhydroxylamine<sup>(16)</sup>. The niobium complex

was dried and weighed as  $\text{NbO}(\text{C}_9\text{H}_8\text{NO}_2)$  and the tantalum precipitate was ignited and weighed as  $\text{Ta}_2\text{O}_5$ .

N-substituted acids form colored hydroxamates which are in many cases soluble in chloroform. Many methods of analysis involving extraction of hydroxamates with chloroform have been developed.

Titanium (IV) has been determined spectrophotometrically with N-benzoylphenylhydroxylamine by quantitatively extracting the 1:1 NBPHA-Ti complex from concentrated hydrochloric acid with chloroform and measuring the absorbance of the solution at a wavelength of 380 m $\mu$  (24). A molar absorptivity of  $6.6 \times 10^3$  was reported for the complex.

Using a similar extraction procedure, N-cinnamoylphenylhydroxylamine has been used to determine vanadium spectrophotometrically at a wavelength of 540 m $\mu$ . Its violet complex had a molar absorptivity of  $6.3 \times 10^3$  in chloroform (22).

N-Furoylphenylhydroxylamine has been reported to form colored complexes with numerous transition metal ions, most of which can be extracted with chloroform (20).

Ordinary monohydroxamic acids have an advantage over the N-substituted variety in that the former are much easier to prepare by the methods previously listed. Numerous cases are reported of gravimetric determinations with these unsubstituted hydroxamic acids. Zirconium (IV) has been quantitatively precipitated with oxalohydroxamic acid (6). Salicylohydroxamic acid forms an orange-colored crystalline precipitate with uranyl (II) which can be weighed after drying at 105° (2). Aluminum, gallium, and indium have been estimated gravimetrically by weighing their respective 1:1 complexes with salicylohydroxamic acid after drying them at 110° (21).

Numerous colorimetric methods of analysis have been developed involving unsubstituted monohydroxamic acids. Complexes formed from these acids and metal ions are not soluble enough in chloroform for chloroform extractions to be performed. Polar oxygenated solvents such as the higher alcohols and esters have been used widely to extract hydroxamates of these acids.

Das Gupta and Singh<sup>(5)</sup> report that the potassium salt of benzo-hydroxamic acid forms a red chelate with vanadium (V) in the pH range 2.7-7.8, the intensity of which can be measured for a colorimetric estimation of vanadium.

Wise and Brandt<sup>(26)</sup> have spectrophotometrically determined vanadium in steels and crude oils with benzohydroxamic acid. By extracting the chelate with 1-hexanol, a molar absorptivity of  $3.5 \times 10^3$  liters/mole-cm. was obtained as compared with the molar absorptivity in water of  $1.0 \times 10^3$  liters/mole-cm. Thus, extraction with 1-hexanol not only concentrates the chelate, but also provides a solvent in which the color of the chelate is more intense.

Uranyl (II) forms a 2:1 ligand to metal complex with benzohydroxamic acid at pH 6.2<sup>(17)</sup>. The golden-colored chelate has been extracted with 1-hexanol and the absorbance measured at 380 mμ.

Iron and manganese have been co-determined in the same sample with anthranilohydroxamic acid by extracting the orange-red iron complex with isobutyl alcohol at a pH of 6.5; adjusting the pH of the aqueous layer to 9.2 or more, and measuring the intensity of the wine-red manganese complex<sup>(9)</sup>.

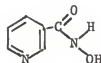
Isonicotinohydroxamic acid,





chelates with copper (II), uranyl (II), cobalt (II), iron (III), and vanadium (V). The latter two metal ions form chelates which obey Beer's law within the range 1-10 gamma/ml<sup>(18)</sup>.

Nicotinohydroxamic acid,



chelates with manganese (III) to form a red-violet chelate at pH values of 9 or above. By measuring the absorbance of its aqueous solution at 480-490 mμ, the manganese ion can be quantitatively determined<sup>(7)</sup>.

Job's method of continuous variations<sup>(12)</sup> suggested a 1:3 ratio of manganese to chelate. Traces of iron have been determined spectrophotometrically as the golden-colored chelate of nicotinohydroxamic acid at a pH of 4.5-6.0 at 440 mμ<sup>(8)</sup>. The iron chelate color is violet for the 1:1 complex, red for the 1:2 complex, and golden for the 1:3 complex. Vanadium and molybdenum both form yellow nicotinohydroxamates at appropriate pH values. Stability constants, pH range, and wavelength of maximum absorption of the vanadium complex have been studied by Polish workers<sup>(18)</sup>. They report that Cu (II), UO<sub>2</sub> (II), Ni (II), and Co (II) also give colored compounds with nicotinohydroxamic acid.

Thiophene-2-hydroxamic acid,



reacts with many metallic ions such as Fe (III), Co (II), Mn (II), Mo (VI), and Nb (V), giving precipitates or soluble compounds<sup>(19)</sup>.

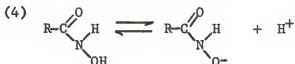
Vanadium (V) forms a violet complex at pH 3.5 with the reagent which has a 3:1 ligand to metal composition. The complex was reported to be extractable from acid solution.

# OBJECTIVES OF THIS INVESTIGATION

The object of the work undertaken in this project was to further study the reactions of unsubstituted monohydroxamic acids with transition metal ions with an eye towards their possible analytical applications.

For the acids selected, it was desired to determine the composition of their more intensely-colored chelates, adherence of the complexes to Beer's law, and whether organic solvents could be utilized to extract the complexes from aqueous solution.

The composition of hydroxamates of various metals is highly dependent on pH. The ionization of the acids as represented below,

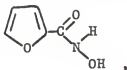


is repressed in acidic solutions making lesser quantities of the free ligand available for complexing than at higher pH values. Thus, higher ligand to metal ratios are obtained as the basicity of the complex solution is increased. For this reason, the pH at which the composition study was made must be specified.

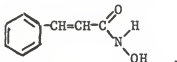
If a chelate is much more soluble in an organic phase than in its aqueous solution, a small amount of the extracting solvent will remove the chelate from a relatively large volume of water. This concentrates the chelate and increases the sensitivity of the metal determination. As mentioned previously, complexes sometimes have higher molar absorptivities in the extractant than in the aqueous layer--another factor which makes extraction procedures practical. By regulation of

the pH of the solution, it is sometimes possible to eliminate interferences with a selective extraction.

The acids studied herein were nicotinohydroxamic acid, the potassium salt of 2-furohydroxamic acid,



and cinnamohydroxamic acid,



The first two compounds listed contain heterocyclic groups and information on the effect of these groups on extraction of the chelates was sought.

The latter compound, cinnamohydroxamic acid, was considered to be of interest because of the extended conjugation in the acid. Compounds with extended conjugation are known to be chromophoric and the longer the conjugated system, the more intense the color<sup>(10)</sup>. Because of this, it was felt that chelates of cinnamohydroxamic acid would be more intensely colored than the corresponding benzohydroxamic acid complexes which have been studied.

#### INVESTIGATION OF METAL-LIGAND CHELATE FORMATION

Initially, solutions of available metal ions were tested for chelation with nicotinohydroxamic acid, cinnamohydroxamic acid, and potassium 2-furohydroxamate in the pH range 0-12 by visually observing any precipitate or color formation when metal and hydroxamic acid were mixed. Nicotinohydroxamic acid is commercially available from Nutritional Biochemicals Co. of Cleveland, Ohio, but cinnamohydroxamic acid and

potassium 2-furohydroxamate had to be prepared according to reaction<sup>(1)</sup>.

#### Preparation of Hydroxamic Acids

Cinnamohydroxamic acid was prepared from ethyl cinnamate in the same manner Blatt<sup>(3)</sup> prepared benzohydroxamic acid from ethyl benzoate.

Methanolic solutions of potassium hydroxide (46.7 g in 240 ml. of methyl alcohol) and hydroxylamine hydrochloride (56.1 g in 140 ml. of methanol) were prepared by dissolving the materials in boiling solvent. The solutions were cooled slowly to room temperature and the hydroxide solution was added with shaking (in an ice bath) to the hydroxylamine hydrochloride solution. The mixture was allowed to stand for five minutes, whereupon ethyl cinnamate (58.7 g) was added with shaking. The mixture was filtered through a Buchner funnel and the residue washed with methyl alcohol. The filtrate was allowed to stand for 48 hours. The crystals formed were filtered and washed with a small amount of methyl alcohol.

The potassium salt obtained above (37.9 g) was stirred and heated with 160 ml. of 1.25 N acetic acid until a clear solution was obtained. This solution was first cooled to room temperature and then with an ice bath. The white crystals obtained here (19.7 g) were filtered, dried, and recrystallized three times from 1:3 water-ethanol solvent. A melting point of 112-113° was obtained for the cinnamohydroxamic acid crystals on a Fisher-Johns melting point apparatus. The melting point listed in the literature is 110-111°<sup>(16)</sup>.

Potassium 2-furohydroxamate was prepared from methyl 2-furoate according to the method of Blatt<sup>(3)</sup>.

Technique and quantities used were the same as in the above described preparation of cinnamohydroxamic acid to the point where methyl 2-furoate (42.0 g) rather than ethyl cinnamate was added to the methanolic  $\text{KOH-NH}_2\text{OH}$  solution. The mixture was allowed to stand for 48 hours. Crystals of the potassium salt (36.2 g) were filtered, dried, and recrystallized three times from water-ethanol solvent. A melting point determination revealed that potassium 2-furohydroxamate decomposes at  $115^\circ$ .

#### Reagents

Aqueous solutions approximately 0.01 M were prepared for available metal ions from analytical grade reagent compounds and the proper solvent to solubilize the metal ions.

Cinnamohydroxamic Acid 0.01 M

Hydrochloric Acid 3 M, 0.1 M

Nicotinohydroxamic Acid 0.01 M

Potassium 2-Furohydroxamate 0.01 M

Sodium Hydroxide 3 M, 0.1 M

#### Experimental

To two ml. of each metal solution prepared, ten ml. of ligand solution was added. The resulting solutions were diluted with 25 ml. of water and stirred with a magnetic stirrer for 5 - 10 minutes. The pH of each solution was adjusted with sodium hydroxide or hydrochloric acid to cover the pH range 0-12 in one unit increments. About five minutes of stirring was allowed between each pH adjustment to allow the metal ion

and ligand to come to equilibrium.

The results of the metal ion-nicotinylhydroxamic acid study are shown in Table I.

Studies on chelates of cinnamohydroxamic acid and potassium 2-furohydroxamate are tabulated in Table II. The chelating characteristics of these two ligands have not been investigated previously as have those of nicotinylhydroxamic acid, so the results are listed in greater detail. As some metal ions possess color prior to chelation and others form hydrated oxides which change color as the pH is varied, a metal ion "blank" was made by noting the color of the metal ion in the absence of any ligand in the pH interval 0-12. This was done by diluting two ml. of metal ion solution with 35 ml. of water, adjusting the pH, and observing the solution color.

#### Discussion of Results

It was found that nicotinohydroxamic acid forms colored chelates with iron (II), iron (III), manganese (II), molybdenum (VI), titanium (IV), uranium (VI), and vanadium (V). The hydroxamates of molybdenum (yellow), titanium (golden), and uranium (yellow) were singled out for further investigation, as they have not been studied very thoroughly previously.

Cinnamohydroxamic acid forms a black precipitate with Au (III), pink precipitates with Ce (III), and Co (II), violet chelates with Ce (IV), Mn (II), V (IV) and (V), a lime-colored precipitate with Cu (II), a violet color or red-orange precipitate with Fe (III), a yellow-green precipitate with Ni (III) and Hg (I), white precipitates

Table 1. Investigation of metal NHA chelate formation

Ion	Compound	Solvent	Results
Ag <sup>+1</sup>	AgClO <sub>4</sub>	Dilute HCl	No apparent chelation
As <sup>+5</sup>	As <sub>2</sub> O <sub>5</sub>	Dilute HCl	No apparent chelation
Cd <sup>+2</sup>	CdCl <sub>2</sub>	Dilute HCl	No apparent chelation
Ce <sup>+4</sup>	Ce(NO <sub>3</sub> ) <sub>4</sub>	Dilute HNO <sub>3</sub>	No apparent chelation
Cr <sup>+3</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub>	Dilute HNO <sub>3</sub>	No apparent chelation
Cr <sup>+6</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Dilute HCl	No apparent chelation
Fe <sup>+2</sup>	FeCl <sub>2</sub>	Dilute HCl	Red soln. for pH 2.5-6.0
Fe <sup>+3</sup>	FeCl <sub>3</sub>	Dilute HCl	Red soln. for pH 2.5-6.0
Ge <sup>+4</sup>	GeCl <sub>4</sub>	Dilute HCl	No apparent chelation
In <sup>+3</sup>	In	Conc. HNO <sub>3</sub>	No apparent chelation
La <sup>+3</sup>	La(Ac) <sub>3</sub>	Dilute HCl	No apparent chelation
Mn <sup>+2</sup>	MnSO <sub>4</sub>	Dilute H <sub>2</sub> SO <sub>4</sub>	Violet soln. for pH 9-12
Mo <sup>+6</sup>	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	Dilute HCl	Yellow soln. for pH 0-8
Ni <sup>+2</sup>	NiCl <sub>2</sub>	Dilute HCl	No apparent chelation
Pb <sup>+2</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	Dilute HNO <sub>3</sub>	No apparent chelation
Rh <sup>+3</sup>	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Dilute HCl	No apparent chelation
Sn <sup>+2</sup>	SnCl <sub>2</sub>	Dilute HCl	No apparent chelation
Te <sup>+4</sup>	TeCl <sub>4</sub>	Dilute HCl	No apparent chelation
Ti <sup>+4</sup>	K <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	Dilute HCl	Golden soln. for pH 3-9
U <sup>+6</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Dilute HNO <sub>3</sub>	Yellow soln. for pH 3-11
V <sup>+5</sup>	NaVO <sub>3</sub>	Dilute HCl	Pink soln. for pH 3-9
W <sup>+6</sup>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	Dilute HCl	No apparent chelation
Y <sup>+3</sup>	Y(NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	Dilute HCl	No apparent chelation
Zr <sup>+4</sup>	ZrO(NO <sub>3</sub> ) <sub>2</sub>	Dilute HNO <sub>3</sub>	No apparent chelation

Table 2. Investigation of metal-K(FHA) and metal-(CHA) chelates

Ion	Compound	pH	Solution of CHA	Solution of K(FHA)	Metal Ion Solution Alone
As <sup>+3</sup>	As <sub>2</sub> O <sub>3</sub>	0-12	-	-	-
As <sup>+5</sup>	As <sub>2</sub> O <sub>5</sub>	0-12	-	-	-
Au <sup>+3</sup>	HAuCl <sub>4</sub> ·3H <sub>2</sub> O	0	black, ppt.	orange, ppt.	yellow
"	"	3	" "	" "	"
"	"	6	" "	golden	"
"	"	9	yellow	"	"
"	"	12	"	"	"
Be <sup>+2</sup>	Be(NO <sub>3</sub> ) <sub>2</sub>	9-12	-	-	-
Cd <sup>+2</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0-12	-	-	-
Ce <sup>+3</sup>	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0	-	-	cloudy
"	"	3	-	-	"
"	"	6	pink, ppt.	-	"
"	"	9	" "	orange	"
"	"	12	" "	"	"
Ce <sup>+4</sup>	Ce(HSO <sub>4</sub> ) <sub>4</sub>	0	yellow	yellow	yellow
"	In H <sub>2</sub> SO <sub>4</sub>	3	-	-	white, ppt.
"	"	6	violet	-	" "
"	"	9	"	orange	" "
"	"	12	violet, ppt.	"	" "
Co <sup>+2</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0	-	-	-
"	"	3	-	-	-
"	"	6	pink, ppt.	pink	-
"	"	9	" "	"	blue
"	"	12	" "	blue-green	"



Table 2. (cont.)

Ion	Compound	pH	Solution of CHA	Solution of K(FHA)	Metal Ion Solution Alone
Cr <sup>+6</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0-12	-	-	yellow
Cu <sup>+2</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	0	-	-	-
"	in HNO <sub>3</sub>	3	lime, ppt.	-	-
"		6	" "	lime, ppt.	blue, ppt.
"		9	" "	" "	" "
"		12	" "	" "	" "
Fe <sup>+3</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0	violet	violet	light yellow
"		3	red-orange, ppt.	red-orange	" "
"		6	" " "	" "	" "
"		9	" " "	" "	" "
"		12	" " "	" "	" "
Hg <sup>+</sup>	Hg(NO <sub>3</sub> )	0-6	-	-	-
"	in HNO <sub>3</sub>	6-12	lime, ppt.	-	-
In <sup>+3</sup>	In(NO <sub>3</sub> ) <sub>3</sub>	0-6	-	-	-
"	in HNO <sub>3</sub>	6-12	white, ppt.	-	-
La <sup>+3</sup>	La(OAc) <sub>3</sub>	0-6	-	-	-
"	in HOAc	6-12	white, ppt.	white, ppt.	cloudy
Mn <sup>+2</sup>	MnSO <sub>4</sub> ·H <sub>2</sub> O	0	" "	-	yellow
"		3	" "	-	"
"		6	brown, ppt.	-	-
"		9	violet	violet	brown, ppt.
"		12	"	"	" "
Mo <sup>+6</sup>	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0	yellow, ppt.	yellow	-
"		3	" "	"	-

Table 2. (cont.)

Ion	Compound	pH	Solution of	Solution of	Metal Ion
			CHA	K(FHA)	Solution Alone
Mo <sup>+6</sup>	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	6	intense yellow	yellow	-
"		9	" "	"	-
"		12	yellow	pale yellow	-
Ni <sup>+2</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0-6	-	-	-
"		6-12	white, ppt.	-	-
Ni <sup>+3</sup>	Ni <sub>2</sub> O <sub>3</sub>	0-6	-	-	-
"	in HCl	6-12	lime, ppt.	lime, ppt.	cloudy
Os <sup>+8</sup>	OsO <sub>4</sub> in	0	brown, ppt.	yellow	-
"	H <sub>2</sub> SO <sub>4</sub>	3	" "	"	-
"		6	orange	orange	-
"		9	intense orange	"	-
"		12	" "	"	-
Pb <sup>+2</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	0-6	-	-	-
"		6-12	white, ppt.	white, ppt.	white, ppt.
Re <sup>+7</sup>	Re <sub>2</sub> O <sub>7</sub>	0-12	-	-	-
Sb <sup>+5</sup>	Sb <sub>2</sub> O <sub>5</sub> in HCl	0-12	white, ppt.	white, ppt.	white, ppt.
Se <sup>+4</sup>	H <sub>2</sub> SeO <sub>3</sub>	0-12	-	-	-
Se <sup>+6</sup>	Na <sub>2</sub> SeO <sub>4</sub>	0-12	-	-	-
Te <sup>+4</sup>	TeO <sub>2</sub> in	0-3	-	-	-
"	HCl	3-6	cloudy	cloudy	cloudy
"		6-12	-	-	-
Te <sup>+6</sup>	H <sub>6</sub> TeO <sub>6</sub>	0-12	-	-	-

Table 2. (cont.)

Ion	Compound	pH	Solution of		Solution of		Metal Ion	
			CHA		K(FHA)		Solution Alone	
Th <sup>+4</sup>	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	0	-		-		-	
"		3	white, ppt.		-		-	
"		6	" "		white, ppt.		-	
"		9	" "		" "		-	
"		12	" "		" "		-	
Ti <sup>+4</sup>	K <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> )·2H <sub>2</sub> O	0	yellow-orange, ppt.		-		cloudy	
"		3	" "		" pale yellow		"	
"		6	" "		" " "		"	
"		9	" "		" yellow "		-	
"		12	yellow, ppt.		yellow		-	
Te <sup>+1</sup>	Te(NO <sub>3</sub> )	0-12	-		-		-	
U <sup>+6</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0	-		-		-	
"		3	orange		faint orange		-	
"		6	intense orange, ppt.		orange, ppt.		yellow, ppt.	
"		9	orange, ppt.		" "		" "	
"		12	" "		faint orange		" "	
V <sup>+4</sup>	VO <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	0	purple, ppt.		-		-	
"		3	" "		yellow-green		light green	
"		6	violet, ppt.		" "		" "	
"		9	violet		light violet		" "	
"		12	-		-		-	

Table 2. (concl.)

Ion :	Compound :	pH :	Solution of :	Solution of :	Metal Ion Solution Alone
			CHA :	K(FHA) :	
V <sup>+5</sup>	Na <sub>3</sub> VO <sub>4</sub> ·16H <sub>2</sub> O	0	intense violet	faint violet	yellow
		3	" "	violet	"
		6	" "	yellow	"
		9	light violet	light violet	"
		12	-	-	"
W <sup>+6</sup>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	0-3	white, ppt.	-	-
		3-12	-	-	-
Y <sup>+3</sup>	Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0-6	-	-	-
		6-12	white, ppt.	white, ppt.	-
Zr <sup>+4</sup>	ZrO(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O in HNO <sub>3</sub>	0-12	white, ppt.	-	-

-denotes no color or precipitate

with IN (III), La (III), Ni (II), Th (IV), W (VI), Y (III) and Zr (IV). The ligand forms an intense yellow precipitate with Mo (VI) and orange chelates with Os (VIII), Ti (IV), and U (VI). The white complexes are obviously not suitable for spectrophotometric study in the visible region and the metal ions in some cases, absorbed in the same region as their chelates--making them unsuitable for spectrophotometric investigation. Cinnamohydroxamates of vanadium, iron, molybdenum, osmium, titanium, and uranium were judged to be of interest for further analytical study.

Potassium 2-furohydroxamate forms a golden-colored chelate with

Au (III), orange complexes with Ce (III) and (IV), Os (VIII), and U (VI), a pink solution with Co (II), a yellow-green precipitate with Cu (II) and Ni (III), violet and red-orange solutions with Fe (III), a white precipitate with La (III), Th (IV), and Y (III), and violet solutions with Mn (II), and vanadium (IV) and (V).

The ligand forms yellow complexes with Mo (VI) and Ti (IV). As a general observation, the chelates of potassium 2-furohydroxamate appeared to be more soluble in water and to possess a less intense color than the corresponding complexes of cinnamohydroxamic acid. Furohydroxamates of uranium, iron, osmium, molybdenum, titanium, and vanadium were considered to be interest for further study.

#### NICOTINOHYDROXAMATES OF Ti (IV), Mo (VI), AND $UO_2$ (II)

##### Effect of pH on Transmittance

Apparatus: Beckman DB spectrophotometer equipped with matched 1.00 cm. cells.

Beckman potentiometric recorder.

Beckman zeromatic pH meter.

Magnetic stirrer.

In order to determine the effect of pH on the transmittance of solutions of titanium (IV), molybdenum (VI), and uranyl (II) nicotinohydroxamates, solutions of each metal chelate were prepared at each pH where any signs of color formation were observed. These solutions were placed in the cell of a Beckman DB spectrophotometer and the spectrum was recorded from 700 m $\mu$  to 320 m $\mu$ . Water was used as the reference solvent. The results (Figure 1) show that the

golden titanium (IV) nicotinohydroxamate has a maximum absorption at 380 m $\mu$  and the best pH range for its formation is a pH of 7-8.

Uranyl (II) nicotinohydroxamate also has a maximum absorption at 380 m $\mu$ . The pH range 6.0-8.0 is the most favorable for formation of the chelate. (Figure 2)

The yellow molybdenum (VI) chelate with nicotinohydroxamic acid has a maximum absorption at 380 m $\mu$ . The chelate forms its most intense color at a pH of 3.0. (Figure 3)

#### Structure Studies

Job's method of continuous variations<sup>(12)</sup> was applied to the titanium (IV), uranyl (II), and molybdenum (VI) complexes with nicotinylhydroxamic acid. See Figure 4.

The results indicated a 1:4 metal to ligand complex for titanium (IV) formed at a pH of 8.0, a 1:2 complex for molybdenum (VI) at a pH of 3.0, and that uranyl (II) forms a 1:2 complex at a pH of 7.0. Since uranium formed a complex with a pinkish color at lower pH values, as well as the more intense yellow chelate in the range 6.0-8.0, continuous variations studies were also made for the complex at pH 3.0. These studies indicated that the chelate species present in the solution at a pH of 3.0 was an equilibrium mixture of 1:1 and 1:2 chelates of nicotinohydroxamic acid.

#### Conformity to Beer's Law

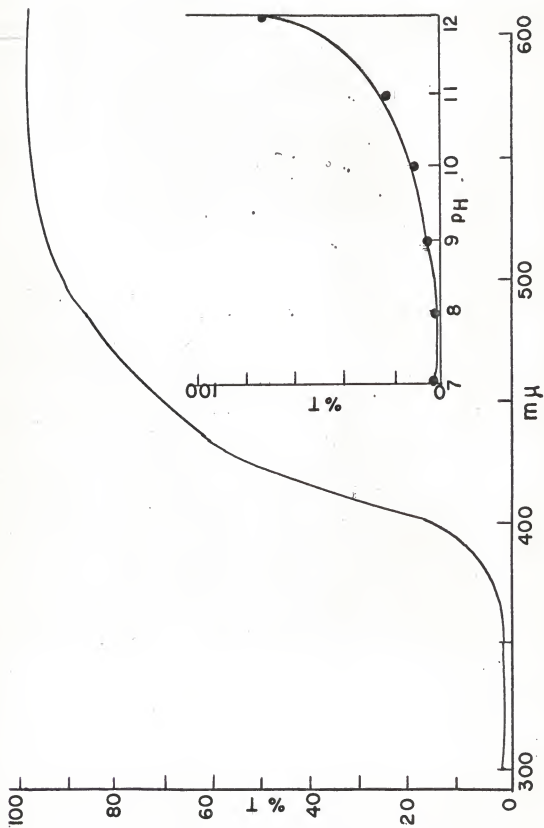
Titanium (IV). In order to ascertain whether the titanium (IV) complex with nicotinylhydroxamic acid conforms to Beer's law, appropriate

EXPLANATION OF FIGURE 1

Fig. 1. Spectrum of titanium (IV) nicotinohydroxamate for approximately  $2.0 \times 10^{-4}$  M solution at pH 7.0.

Inset shows effect of pH on transmission of chelate at 380 m $\mu$ .

FIGURE 1





EXPLANATION OF FIGURE 2

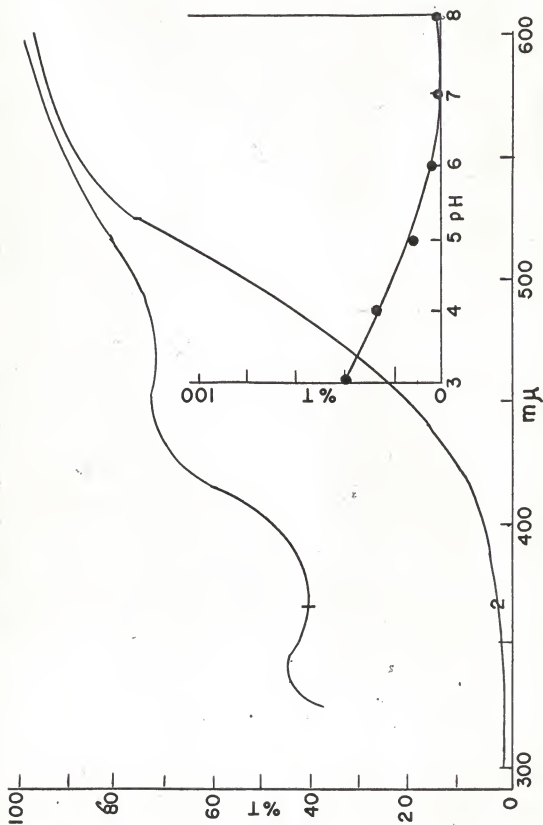
Fig. 2. Spectra of uranyl (II) nicotinohydroxamate for approximately  $2.0 \times 10^{-4}$  M solution.

Spectrum 1 is for solution having pH 3.0.

Spectrum 2 is for solution having pH 7.0.

Inset shows effect of pH on transmission of chelate at 380 m $\mu$ .

FIGURE 2

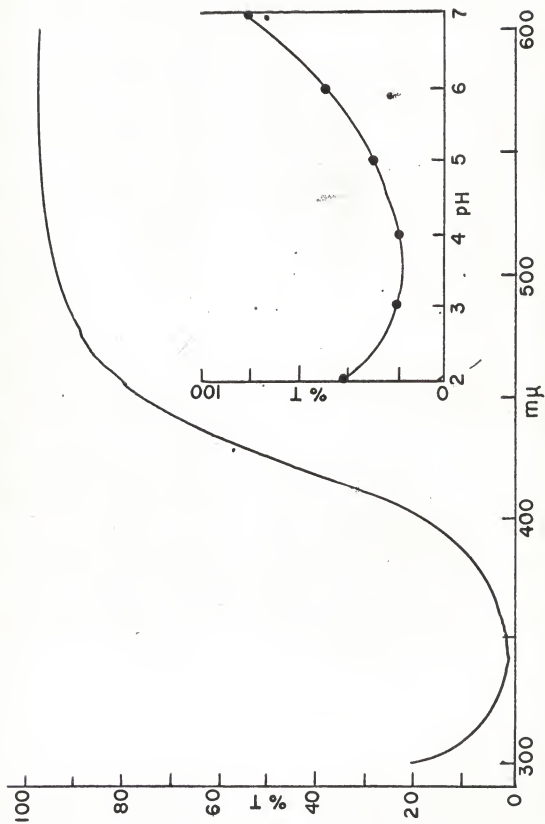


EXPLANATION OF FIGURE 3

Fig. 3. Spectrum of molybdenum (VI) nicotinohydroxamate for approximately  $2.0 \times 10^{-4}$  M solution at pH 3.0.

Inset shows effect of pH on transmission of chelate at 380 m $\mu$ .

FIGURE 3



#### EXPLANATION OF FIGURE 4

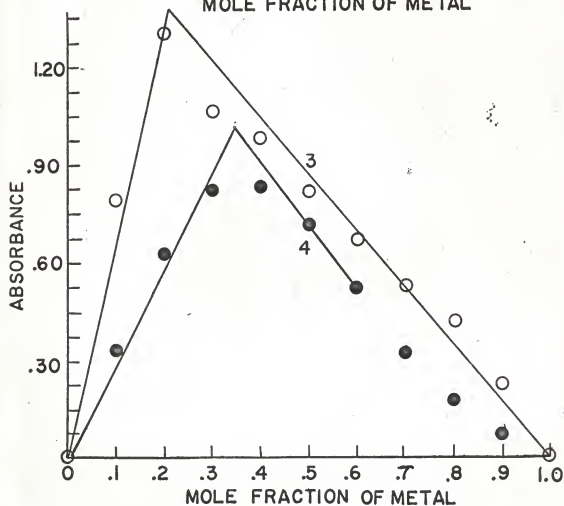
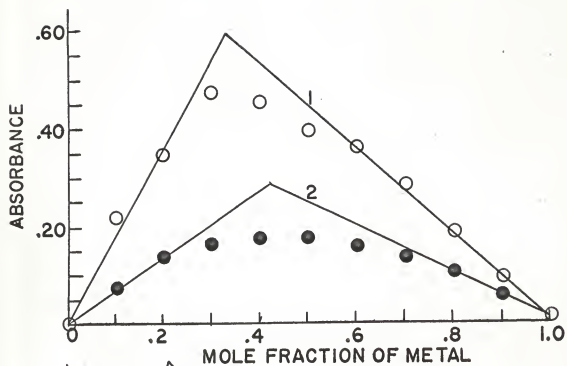
Fig. 4. Continuous variations plots for various nicotinohydroxamates.

Plot 1 is for molybdenum (VI) nicotinohydroxamate at 380 m $\mu$  and pH 3.0.

Plot 2 is for uranyl (II) nicotinohydroxamate at 380 m $\mu$  and pH 3.0.

Plot 3 is for titanium (IV) nicotinohydroxamate at 380 m $\mu$  and pH 8.0.

Plot 4 is for uranyl (II) nicotinohydroxamate at 380 m $\mu$  and pH 7.0.



aliquots of titanium solution were pipeted into 50 ml. volumetric flasks. To this was added 10 ml. of 0.01 M nicotinyldihydroxamic acid and a predetermined quantity of sodium hydroxide solution so that when diluted to volume, the pH of the resulting solutions was 8.0. The volumetric flasks were shaken and the contents were placed in beakers and stirred for five minutes with the aid of a magnetic stirrer. The absorbance of each solution was read at 380 m $\mu$  with a spectrophotometer using water as the reference solution.

The titanium complex followed Beer's law in the concentration range studied and had a molar absorptivity of  $4.9 \times 10^3$  (Figure 5). Of the three nicotinyldihydroxamates studied, the titanium (IV) complex formed by far the most intense color.

Uranyl (II). In a similar manner to the above description, aliquots of uranyl nitrate were diluted to a 50 ml. volume such that the pH of the resulting solutions was 7.0. After stirring, the absorbance was read at 380 m $\mu$ . This complex appears to conform to Beer's law in the concentration range studied and possesses a molar absorptivity of  $1.99 \times 10^3$  for a  $2.0 \times 10^{-4}$  M uranium solution.

Molybdenum (VI). Molybdenum nicotinyldihydroxamate solutions were prepared of various concentrations at a pH of 3.0. The solutions were stirred, placed in the cell of a spectrophotometer and the absorbance read at a wavelength of 380 m $\mu$ . The results (Figure 5) indicate that there is a negative deviation from Beer's law. No doubt this deviation could be eliminated by using more reagent. (The ratio of reagent to metal ion at the highest concentration of molybdenum tested was only 4:1.) However, not enough ligand was available for further work.

EXPLANATION OF FIGURE 5

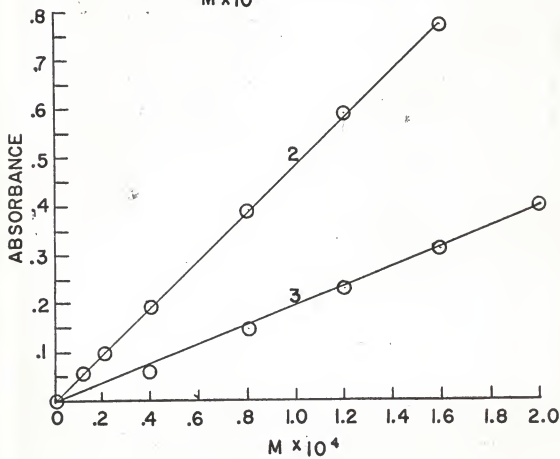
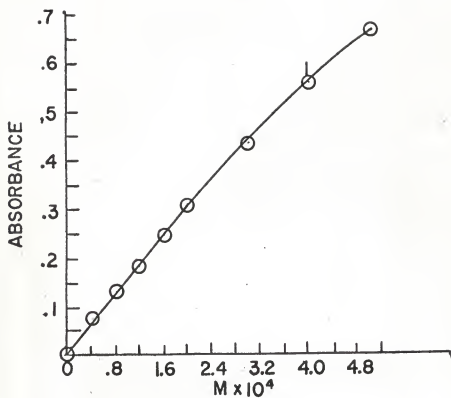
Fig. 5. Beer's law plots for  $\text{UO}_2$  (II), Mo (VI), and Ti (IV) nicotinohydroxamates

Plot 1 is for Mo (VI) nicotinohydroxamate at 380 m $\mu$  and pH 3.0.

Plot 2 is for Ti (IV) nicotinohydroxamate at 380 m $\mu$  and pH 8.0.

Plot 3 is for  $\text{UO}_2$  (II) nicotinohydroxamate at 380 m $\mu$  and pH 7.0.





### Solubility of Nicotinohydroxamates in Organic Solvents

As metal-benzohydroxamic acid chelates have been extracted successfully with 1-hexanol (26, 17) and nicotinohydroxamic acid is similar in structure to benzohydroxamic acid, an attempt was made to find an organic solvent which would quantitatively extract one or more of the chelates.

Solutions of the nicotinohydroxamates of titanium, uranium, and molybdenum were prepared by adding 10 ml. of 0.01 M nicotinohydroxamic acid to one ml. of 0.01 M metal solution, diluting with 25 ml. of water, adjusting to the proper pH with sodium hydroxide or hydrochloric acid, and stirring for approximately 5 minutes. The solutions were placed in 125 ml. separatory funnels, 10 ml. of organic solvent added, and the funnels and contents were shaken well. The funnels were allowed to stand until separation of the aqueous and organic layers occurred. Visual examination revealed that none of the organic solvents would extract those chelates tested. The results of the investigation are summarized in Table 3.

### Interferences

R. L. Dutta<sup>(7)</sup> has extensively studied the effect of foreign ions on the manganese complex with nicotinohydroxamic acid. He found that copper, nickel, cobalt, silver, and mercury interfered but could be rendered soluble and colorless by masking with cyanide solution and potassium iodide solution. Iron was found to interfere with the manganese determination at all concentration levels and had to be

Table 3. Extraction studies on nicotinohydroxamic acid chelates

Solvent employed	Mo (VI)	U (VI)	Ti (IV)
	at pH of 3,6,9	at pH of 3,6,9	at pH of 8
benzene	-	-	-
bromethane	-	-	-
carbon tetrachloride	-	-	-
chloroform	-	-	-
diethyl ether	-	-	-
di-isobutyl ketone	-	-	-
ethyl acetate	-	-	-
ethyl benzoate	-	-	-
heptaldehyde	-	-	-
n-hexanol	-	-	-
isoamyl alcohol	-	-	-
skelly B	-	-	-
toluene	-	-	-

- denotes no visible extraction of the nicotinohydroxamate into the organic layer

removed prior to the determination. Ions like sulfate, nitrate, chloride, acetate, carbonate, thiocyanate, iodide, and thiosulfate were found not to interfere even when present in large amount. Dutta found that a trace of hydrogen peroxide hastened color formation, whereas excess hydrogen peroxide caused destruction of the chelate due to oxidation of the nicotinyhydroxamic acid. Borate, phosphate, tartrate, and oxalate ions did not interfere up to concentrations of 1,000 p.p.m.

Since the molybdenum (VI), uranyl (II), and titanium (IV) nicotino-hydroxamates all have a maximum absorption at 380 m $\mu$ , it is apparent that in addition to the above interferences, any one of these three metal ions must be determined in the absence of the other two.

## 2-FUROHYDROXAMATES

### Effect of pH on Transmittance

The apparatus and procedure here were the same as for the nicotino-hydroxamate study on effect of pH on transmission. Potassium 2-furo-hydroxamate itself appears to absorb at wavelengths shorter than 370 m $\mu$ .

Titanium (IV). Titanium furohydroxamate, a yellow complex, has an absorption maximum at 370 m $\mu$ . Measurements of transmission below 370 m $\mu$  will include absorption due to the ligand, so 370 m $\mu$  is the lower limit of wavelength at which absorbance of furohydroxamates can be measured. A pH of 9.0 is the most favorable for maximum color formation in the titanium complex. See Figure 6.

Uranyl (II). The yellow uranium complex has an absorption maximum at 380 m $\mu$  and a pH of 8.0 is the best for intense color formation. See Figure 7.

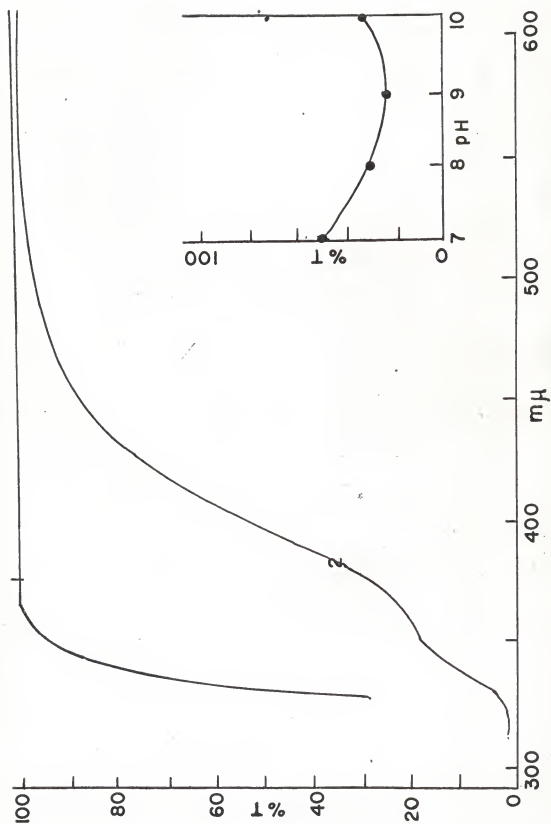
EXPLANATION OF FIGURE 6

Fig. 6. Spectra of potassium 2-furohydroxamate and titanium (IV) furohydroxamate

Spectrum 1 is for potassium 2-furohydroxamate solution (approximately  $2.0 \times 10^{-4}$  M) at pH 9.0.

Spectrum 2 is for titanium (IV) furohydroxamate solution (approximately  $2.0 \times 10^{-4}$  M) at pH 9.0.

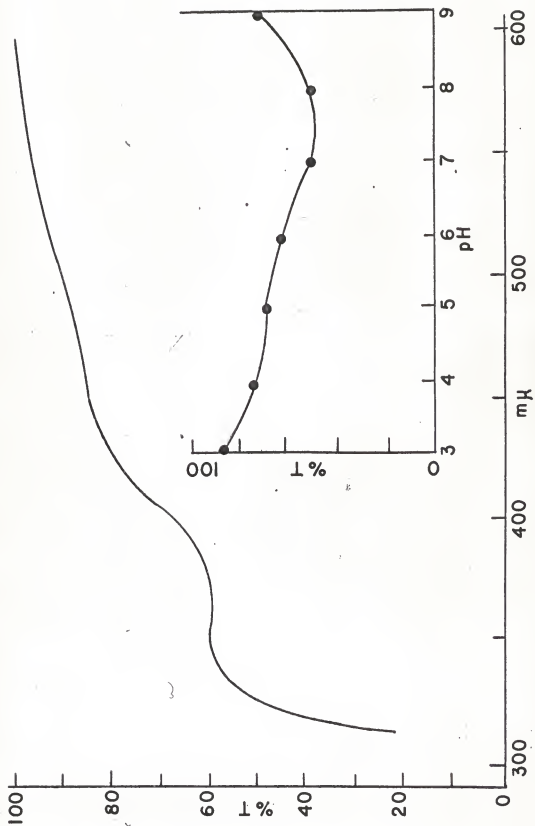
Inset shows effect of pH on transmission of chelate at 370 m $\mu$ .



EXPLANATION OF FIGURE 7

Fig. 7. Spectrum of uranyl (II) furohydroxamate (approximately  $2.0 \times 10^{-4}$  M) solution at pH 8.0.

Inset shows effect of pH on transmission of chelate at 380 m $\mu$ .





Vanadium (V). Vanadium forms a violet complex which has an absorption maximum of 540 m $\mu$  and attains maximum absorption at a pH of 8.0. See Figure 8.

Osmium (VIII). Osmium forms an intense yellow-colored furohydroxamate with an absorption maximum at 390 m $\mu$ . A pH value of 12.0 proves to be the best for osmium-K(FHA) color formation. See Figure 9.

Iron (III). For iron, the wavelength of maximum absorption varies with pH. The violet chelate formed at pH 0 has an absorption maximum at 370 m $\mu$  while the red-orange complex formed at pH 2.0 absorbs most at 500 m $\mu$ . The yellow-orange chelate formed at pH 5.0 has an absorption maximum at 450 m $\mu$ . See Figure 10.

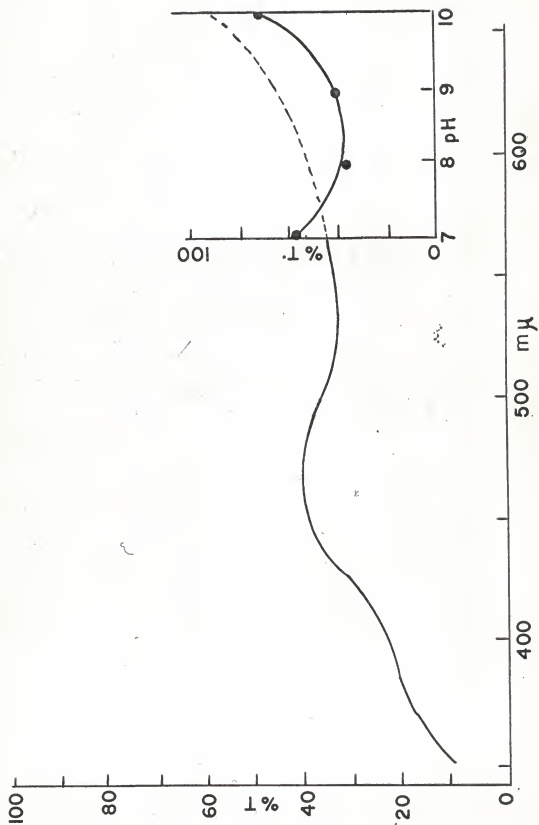
#### Conformity to Beer's Law

Titanium (IV). To determine whether titanium furohydroxamate conforms to Beer's law, aliquots of titanium solution made from a 0.01 M stock solution were pipeted into a 25 ml. volumetric flask. To this was added 10 ml. of 0.01 M potassium 2-furohydroxamate and a pre-determined quantity of sodium hydroxide solution, so that when diluted to volume, the pH of the resulting solutions was 9.0. The volumetric flasks were shaken and the contents placed in beakers and stirred for five minutes with a magnetic stirrer. The percent transmission of each solution was read at 370 m $\mu$  with a spectrophotometer using water as the reference solution. The titanium complex followed Beer's law in the concentration range 1.2 to  $10 \times 10^{-5}$  M and showed a slight negative deviation at higher concentrations than this. A molar

EXPLANATION OF FIGURE 8

Fig. 8. Spectrum of vanadium (V) furohydroxamate (approximately  $2.0 \times 10^{-4}$  M) solution at pH 8.0.

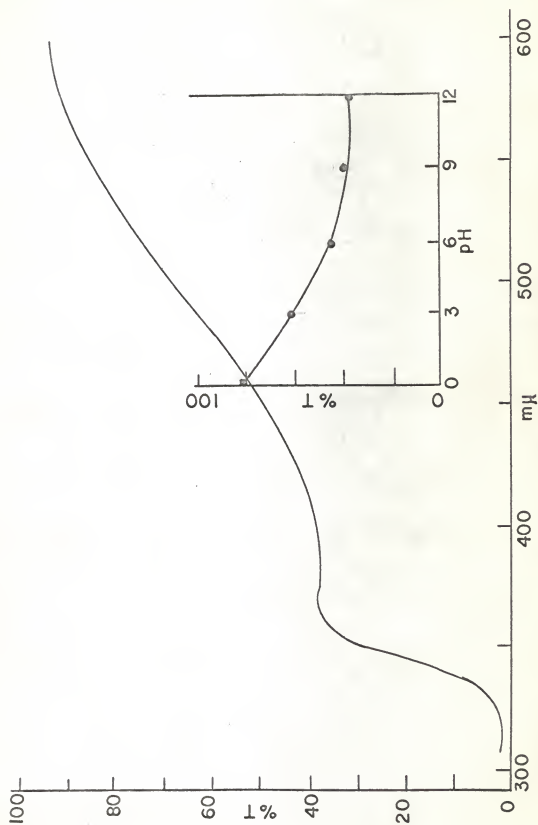
Inset shows effect of pH on transmission of chelate at 540 m $\mu$ .



EXPLANATION OF FIGURE 9

Fig. 9. Spectrum of osmium (VII) furohydroxamate (approximately  $2.0 \times 10^{-4}$  M) solution at pH 12.0.

Inset shows effect of pH on transmission of chelate at 390 m $\mu$ .

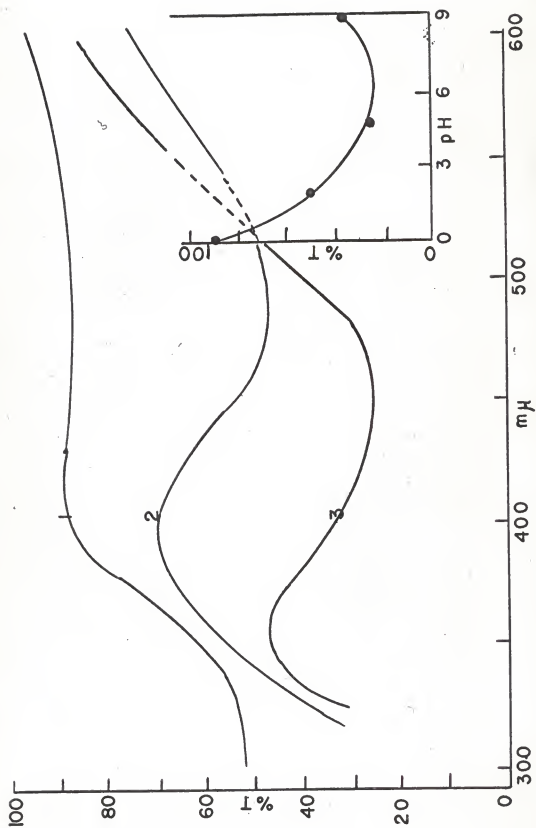


EXPLANATION OF FIGURE 10

Fig. 10. Spectra of iron (III) furohydroxamate (approximately  $2.0 \times 10^{-4}$  M) solutions at various pH values.

- Spectrum 1 is for iron (III) furohydroxamate at pH 0.
- Spectrum 2 is for iron (III) furohydroxamate at pH 2.0.
- Spectrum 3 is for iron (III) furohydroxamate at pH 5.0.

Inset shows effect of pH on transmission of chelate at 450 m $\mu$ .



absorptivity of  $7.17 \times 10^3$  was observed for the complex at a titanium concentration of  $1.0 \times 10^{-4}$  M. See Figure 11.

Vanadium (V). A procedure similar to the above was used to test the adherence of the vanadium-K(FHA) complex to Beer's law. Potassium 2-furohydroxamate (10 ml. of 0.1 M) was added to appropriate aliquots of the vanadium solution. Sodium hydroxide was added so that the pH of the 25 ml. of chelate solution would be 8.0, and the transmission of the solution was measured at 540 m $\mu$  using water as the blank. The complex followed Beer's law in the concentration range  $0.2 \times 10^{-4}$  M to  $3.20 \times 10^{-4}$  M of vanadium and had a molar absorptivity of  $2.99 \times 10^3$  at a vanadium concentration of  $3.20 \times 10^{-4}$  M. See Figure 11.

Uranyl (II). A procedure identical to the above was used to test the adherence to Beer's law of the golden uranyl (II) furohydroxamate at 380 m $\mu$ . Sodium hydroxide solution was added in sufficient quantity so that the pH of the 25 ml. final volume was 7.0. Beer's law was followed in the concentration range studied. ( $0.4 \times 10^{-4}$  M to  $6.0 \times 10^{-4}$  M). The complex had a molar absorptivity of  $2.17 \times 10^3$  for the concentration  $2.0 \times 10^{-4}$  M. See Figure 11.

Iron (III). Similarly, the orange iron-K(FHA) chelate had absorbance values directly proportional to concentration in the concentration range studied. ( $0.4 \times 10^{-4}$  M to  $4.0 \times 10^{-4}$  M). Solutions of appropriate concentration were prepared at pH 5.0 and the transmission was read at 450 m $\mu$ . A molar absorptivity of  $1.86 \times 10^3$  was found for the complex in a  $4.0 \times 10^{-4}$  M solution. See Figure 11.



#### EXPLANATION OF FIGURE 11

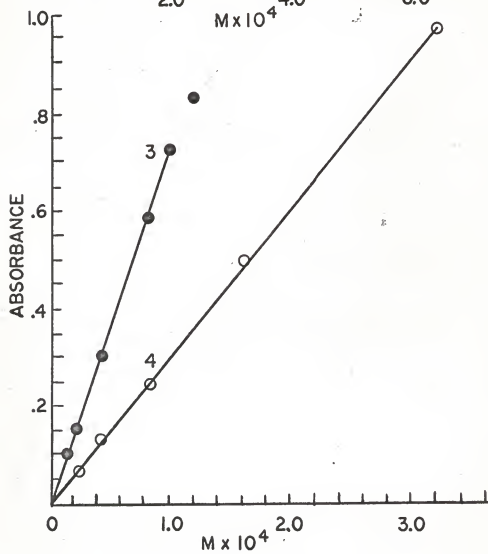
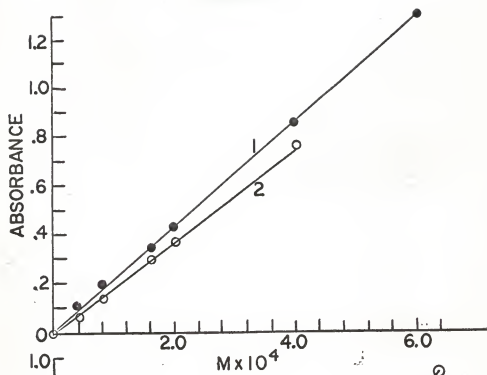
Fig. 11. Beer's law plots for various furohydroxamates.

Plot 1 is for  $\text{UO}_2$  (II) furohydroxamate at 380 m $\mu$  and pH 7.0.

Plot 2 is for Fe (III) furohydroxamate at 450 m $\mu$  and pH 5.0.

Plot 3 is for Ti (IV) furohydroxamate at 370 m $\mu$  and pH 9.0.

Plot 4 is for V (V) furohydroxamate at 540 m $\mu$  and pH 8.0.



### Structure Studies

Job's method of continuous variations<sup>(12)</sup> was applied to the furohydroxamates of titanium (IV), osmium (VIII), iron (III), and vanadium (V) to determine the composition of the chelates.

Titanium (IV). A composition study on titanium (IV) showed that a 4:1 ligand to metal complex existed at pH 9.0. The percent transmission of the solution was measured at 410 m $\mu$  and 460 m $\mu$ . The continuous variations plot is shown in Figure 12.

Osmium (VIII). A similar study on osmium (VIII) at pH 6.0 showed that the osmium furohydroxamate consists of two ligand groups per metal ion. Measurements were made at 380 m $\mu$  and 450 m $\mu$ . See Figure 12.

Iron (III). A continuous variations investigation of the red-orange iron complex at pH 2.0 showed an apparent equilibrium mixture of 1:1 and 2:1 ligand to metal complexes to be present. The wavelength selected for the measurements was 500 m $\mu$ . See Figure 12.

Vanadium (V). Vanadium formed what appeared to be a 4:1 complex with potassium 2-furohydroxamate at pH 8.0. The maximum absorbance of chelate solution corresponded to a metal ion mole fraction of 0.2. It must be mentioned that the metal ion absorbed in the region the absorbance of the chelate was measured. Thus, the results were not as clear-cut as in the other composition studies. See Table 4.

### Solubility of CHA and K(FHA) Complexes in Organic Solvents

Ligand solution (10 ml. of 0.01 M) was added to vanadium (V) (1 ml. of 0.01 M) in a 100 ml. beaker. The solution was diluted to 35 ml.,

#### EXPLANATION OF FIGURE 12

Fig. 12. Continuous variations plots for various furohydroxamates.

Plot 1 is for osmium (VIII) furohydroxamate at 380 m $\mu$  and pH 6.0.

Plot 2 is for osmium (VIII) furohydroxamate at 450 m $\mu$  and pH 6.0.

Plot 3 is for titanium (IV) furohydroxamate at 410 m $\mu$  and pH 9.0. Abscissa represents mole fraction of Ti (IV).

Plot 4 is for iron (III) furohydroxamate at 500 m $\mu$  and pH 2.0. Abscissa represents mole fraction of ligand.

Plot 5 is for titanium (IV) furohydroxamate at 460 m $\mu$  and pH 9.0. Abscissa represents mole fraction of Ti (IV).

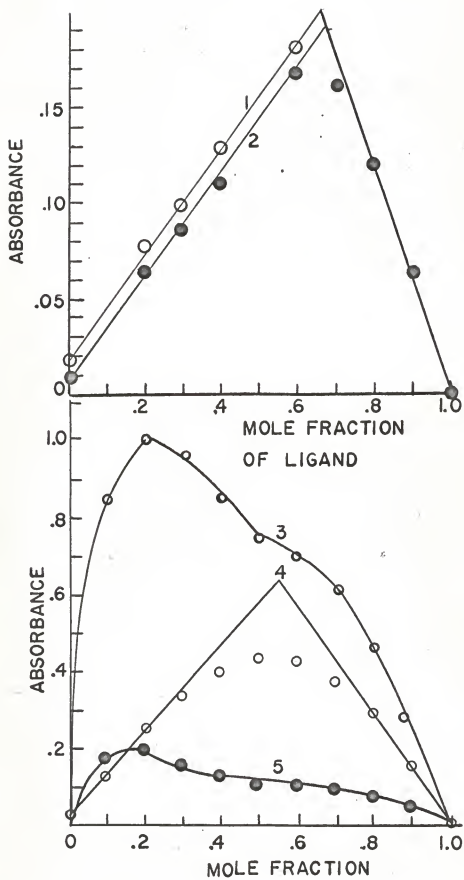


Table 4. Continuous variation study on V (V)-K(FHA) chelate at pH 8.0 using 0.01 M reagents and 10 ml. total volume

Mole fraction K(FHA)	Mole fraction $V^{+5}$	A 520 m $\mu$	A 580 m $\mu$	A 630 m $\mu$
0	10	.035	.000	.000
1	9	.042	.004	.001
2	8	.057	.011	.007
3	7	.064	.036	.021
4	6	.084	.060	.036
5	5	.114	.091	.058
6	4	.154	.127	.081
7	3	.173	.142	.092
8	2	.228	.194	.124
9	1	.156	.142	.097
10	0	.001	.000	.000

the pH was adjusted to 2.0, and the solution was stirred for five minutes. Solvent (10 ml.) was added to the contents of the beaker and the system was stirred for several minutes. After allowing the two phases to separate, the organic layer was then examined visually for any color extracted from the aqueous phase. The results are summarized in Table 5.

Polar, oxygenated solvents were found to be capable of extracting the vanadium complexes of the two ligands from aqueous solution. Cyclohexanone, hexanol, isoamyl alcohol, and octanol removed all the color from the aqueous solution for the vanadium-CHA complex, while ethyl acetate would only partially extract the chelate. Cyclohexanone, 1-hexanol, isoamyl alcohol, and 1-octanol appeared to completely extract vanadium furohydroxamate. Octanol was chosen as the solvent to use for more detailed study on the extraction of chelates of the two ligands.

Table 5. Extraction study on complexes of vanadium (V) with cinnamohydroxamic acid and potassium 2-furohydroxamate

Solvent	Solubility of K(FHA)-V <sup>+5</sup> Complex	Solubility of CHA-V <sup>+5</sup> Complex
benzene	-	-
carbon tetrachloride	-	-
chloroform	-	-
cyclohexane	-	-
cyclohexanone	+	+
di-isobutyl ketone	-	+
ethyl acetate	-	+
1-hexanol	+	+
isoamyl alcohol	+	+
1-octanol	+	+
xylene	-	-

- denotes no color in the organic layer.

+ indicates intense color in the organic layer.

#### Extraction of Vanadium Furohydroxamate with 1-Octanol

The alcohol, 1-octanol, quantitatively extracts vanadium (V) furohydroxamate at pH 3.0 from aqueous solution. See Figure 13 for effect of pH on extraction. The alcoholic solution of chelate followed Beer's law from 1.0 to  $20.0 \times 10^{-5}$  moles of chelate/liter of octanol and had a molar absorptivity of  $2.60 \times 10^3$  at a concentration of  $2.0 \times 10^{-4}$  M. See Figure 13. This is slightly less than the molar absorptivity in water ( $3.1 \times 10^3$  for the aqueous solution) but the extraction process concentrates the chelate by a factor of five--a factor which compensates for the lower molar absorptivity. Qualitative tests showed that iron, molybdenum, uranium, and titanium would also form chelates that would extract at this pH.

#### EXPLANATION OF FIGURE 13

Fig. 13. Effect of pH on extraction of vanadium (V) furohydroxamate. Beer's law plots for cinnamohydroxamates and furohydroxamates.

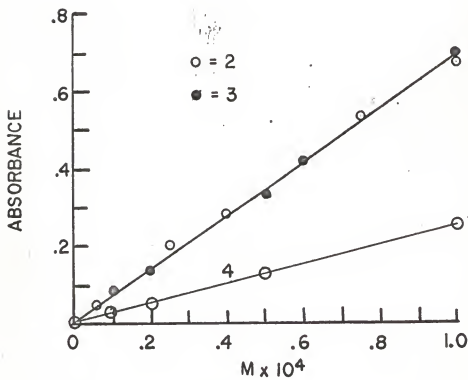
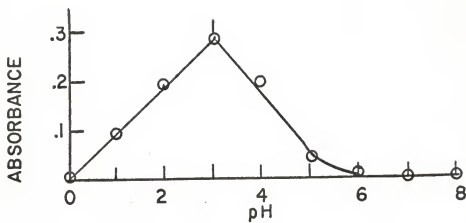
Plot 1 shows effect of pH on absorbance of vanadium (V) furohydroxamate extracted with 1-octanol.

Plot 2 shows that Beer's law is followed by uranyl (II) cinnamohydroxamate extracted into 1-octanol.

Plot 3 shows that Beer's law is followed by vanadium (V) cinnamohydroxamate extracted into 1-octanol.

Plot 4 shows that Beer's law is followed by vanadium (V) furohydroxamate extracted into 1-octanol.





It was necessary to distil the alcohol prior to using it for extraction, as peroxides have been reported to form in alcohols. These peroxides react with hydroxamic acid chelates and destroy the color<sup>(17)</sup>, so it is necessary to remove them if any reproducible extraction data are to be obtained. After distillation, the octanol was saturated with water and stored in a brown bottle.

To test for completeness of extraction, aliquots of  $1.0 \times 10^{-4}$  M  $V^{+5}$  were pipeted into a 100 ml. beaker, K(FHA) added (10 ml. of 0.01 M), and the total volume and pH adjusted to 50 ml. and 3.0, respectively. The solutions were stirred for about five minutes with a magnetic stirrer and 10 ml. of 1-octanol was added to the beaker. This two-phase system was stirred for another five minutes and transferred to a 125 ml. separatory funnel. The funnel was shaken several times and allowed to stand until complete separation of the two phases had occurred. The aqueous phase was drained off through the stopcock and the organic phase poured out through the top of the funnel. The extract was centrifuged for 5-10 minutes to further remove water from the organic extract and the percent transmission of the complex was read at 450 m $\mu$  using octanol as the blank.

#### CINNAMOHYDROXAMATES

##### Effect of pH on Transmittance

Cinnamohydroxamic acid absorbs in the visible region as shown in Figure 14. A 0.002 M solution of cinnamohydroxamic acid absorbs radiation in the wavelength region 370 m $\mu$  and below when the pH is 6.2. Thus, any

EXPLANATION OF FIGURE 14

Fig. 14. Spectra of cinnamohydroxamic acid  
(approximately  $2.0 \times 10^{-3}$  M) solution  
at various pH values.

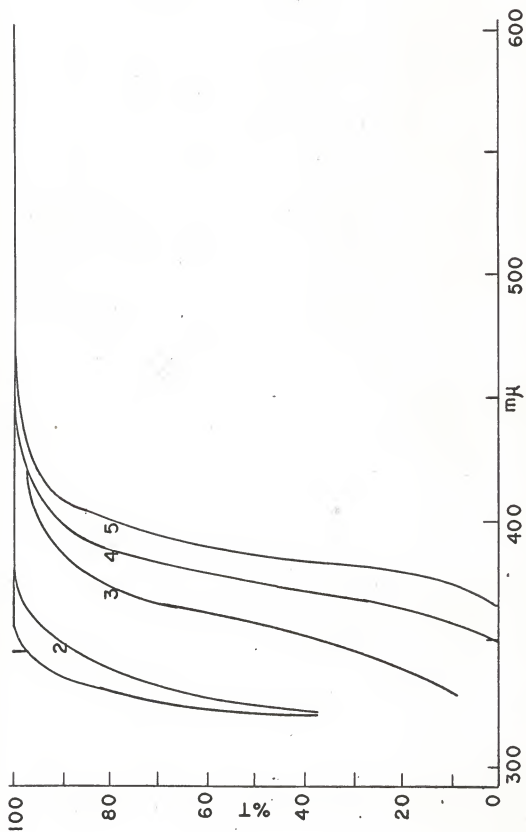
Spectrum 1 is for solution at pH 2.0.

Spectrum 2 is for solution at pH 6.2.

Spectrum 3 is for solution at pH 7.0.

Spectrum 4 is for solution at pH 8.0.

Spectrum 5 is for solution at pH 9.0.



absorbance measurements on its chelates must be done at pH values 6.2 and lower or at considerably higher wavelengths where the ligand does not absorb. At higher pH values, the ligand starts absorbing at wavelengths as high as 440 m $\mu$ .

As the cinnamohydroxamates are not as soluble in water solution as are the furohydroxamates, their spectra were not examined in aqueous solution.

#### Effect of pH on Extraction of Cinnamohydroxamates with 1-Octanol

To determine the effect of pH on extraction of the metal chelates, 1 ml. of 0.01 M metal ion solution was pipeted into a 100 ml. beaker. Ligand was added by pipet (10 ml. of 0.01 M CHA), the solution was diluted to approximately 50 ml., and the pH was adjusted to the desired value. The solution was stirred to attain maximum color formation and 1-octanol (10 ml.) was pipeted into the beaker and stirred for about five minutes. The remainder of the procedure is identical to that used in determining the effect of pH on extraction of chelates of potassium 2-furohydroxamate.

Vanadium (V). Figure 15 shows that the vanadium-CHA complex extracts best in the pH region 2-6. From pH 6.0 to 8.0, the absorbance of the chelate solutions falls off rapidly until pH 9.0 where the complex does not absorb at all at 460 m $\mu$ . The vanadium complex is rather unique in that it has significant color in strongly acidic solution. The extracted species has an absorption maximum at 460 m $\mu$ .

Uranyl (II). Uranyl (II) cinnamohydroxamate, when extracted from aqueous solutions of pH 0-2 does not absorb at 380 m $\mu$ . Figure 15 reveals

that the complex can be most successfully extracted at pH 5.0 and 9.0.

Iron (III). Absorbance of the iron (III) chelate measured at 440 m $\mu$  rises steadily after pH 0 and reaches a maximum at pH 2.0. At pH values 3.0 and higher, the absorbance levels off. See Figure 15.

Titanium (IV). The extracted titanium cinnamohydroxamate absorbs in the entire pH range studied (0-7). The absorbance of the yellow extract was measured at 380 m $\mu$ . See Figure 15.

Of the metal ions studied, vanadium forms the most intensely colored chelate in octanol. The high absorbance of the vanadium-CHA complex at pH 0.0 led to the belief that by lowering the pH of the solution to even more acidic values, vanadium could be extracted with no interferences from other ions.

Iron (III) is the interfering ion most desired to eliminate. Wise and Brandt<sup>(26)</sup> found it necessary to reduce iron (III) on a mercury cathode prior to determining vanadium in steels and crude oils spectrophotometrically with benzohydroxamic acid.

As can be seen in Figure 15, the absorbance of iron cinnamohydroxamate falls off rapidly at pH values below 2.0. It was felt that vanadium could be determined in the presence of iron by extraction from extremely acidic solutions. Experimentation showed that in solutions acidic enough to prevent extraction of iron, the vanadium complex extracted possessed very little or no color at all. So, this attempt proved to be unfruitful.

No doubt electrolysis with a mercury pool would eliminate iron as an interference as it did in the case of the benzohydroxamic acid chelate.

#### EXPLANATION OF FIGURE 15

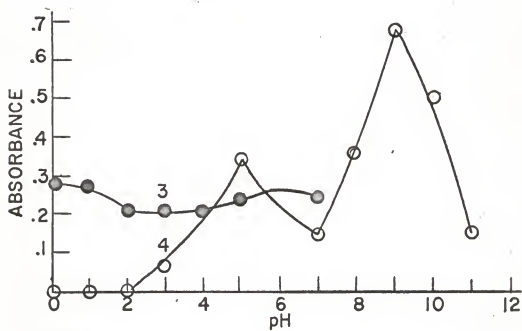
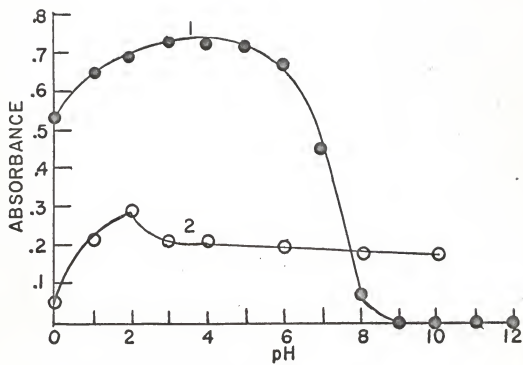
Fig. 15. Effect of pH on absorbance of various cinnamohydroxamates extracted into 1-octanol.

Plot 1 is for vanadium (V) cinnamohydroxamate extracts measured at 460 m $\mu$ .

Plot 2 is for iron (III) cinnamohydroxamate extracts measured at 440 m $\mu$ .

Plot 3 is for titanium (IV) cinnamohydroxamate extracts measured at 380 m $\mu$ .

Plot 4 is for uranyl (II) cinnamohydroxamate extracts measured at 380 m $\mu$ .





### Beer's Law Studies on Cinnamohydroxamates in Octanol

The procedure used was the same as for the Beer's law studies on furohydroxamates. For the uranyl (II) extract, it was necessary to prepare a blank by extracting the ligand alone from an aqueous solution of pH 9.0. High absorbance values would be obtained for the uranium chelate if the blank were not prepared in this manner, as the ligand is extracted and absorbs in basic solution. Octanol was used as the blank for the vanadium complex extraction.

Uranyl (II). Uranium cinnamohydroxamate of varying concentrations was extracted at pH 9.0 from aqueous solutions and the absorbance of the extract was measured at 380 m $\mu$ . The chelate appears to follow Beer's law in the concentration range  $0.5$  to  $10.0 \times 10^{-5}$  M (in octanol) and has a molar absorptivity in octanol of  $6.7 \times 10^3$ . See Figure 13.

Vanadium (V). Vanadium (V) cinnamohydroxamate of varying concentrations was extracted at pH 2.0 with octanol and the absorbance was measured at 460 m $\mu$ . Beer's law was followed in the range  $1.0$  to  $10.0 \times 10^{-5}$  M (in octanol) and the complex had a molar absorptivity of  $7.0 \times 10^3$ . See Figure 13. No doubt the negative deviation from linearity in the higher concentration range could be remedied by using a greater quantity of reagent. The molar absorptivity of the vanadium cinnamohydroxamic acid complex is exactly double that of the corresponding benzohydroxamic acid complex. So, this reagent could be substituted for benzohydroxamic acid in the determination of vanadium in steel and crude oil in order to increase the sensitivity of the determination.

### Structure Study

Iron (III). At pH 2.0, the pH at which iron cinnamohydroxamate best extracts into 1-octanol, iron forms its most intense color with cinnamohydroxamic acid when the concentrations of ligand and metal are identical. See Figure 16. At this pH then, the complex apparently has a ligand to metal ratio of 1:1. The wavelength selected for the continuous variations study was 510 m $\mu$ .

Uranyl (II). Continuous variations studies were made on uranium cinnamohydroxamate at pH 4.0 and 5.0, measuring the absorbance of the solutions at 380 m $\mu$ . As mentioned earlier, the absorbance of the 1-octanol extract is highest at pH 9.0 for the uranium chelate. However, as uranyl (II) forms oxides in basic solution which possess a more intense color than in neutral or acidic solution<sup>(25)</sup>, the lower pH values were selected for the study. One of the requisites for a continuous variations study is that neither ligand nor metal alone should absorb in the wavelength region at which the absorbance of the chelate is being measured. At pH values of 4.0 and 5.0, the highest absorbance value of the aqueous chelate solutions occurred at a mole fraction of ligand of 0.6. See Figure 16. This indicates the presence of a mixture of 1:1 and 2:1 ligand to metal chelates.

### Effect of Ligand to Metal Ratio

Vanadium (V) solution (1 ml. of 0.001 M) was pipeted into a 100 ml. beaker and cinnamohydroxamic acid of varying quantities was added to this. The solutions were diluted to approximately 50 ml., the pH adjusted to 2.0, and were stirred for about five minutes.

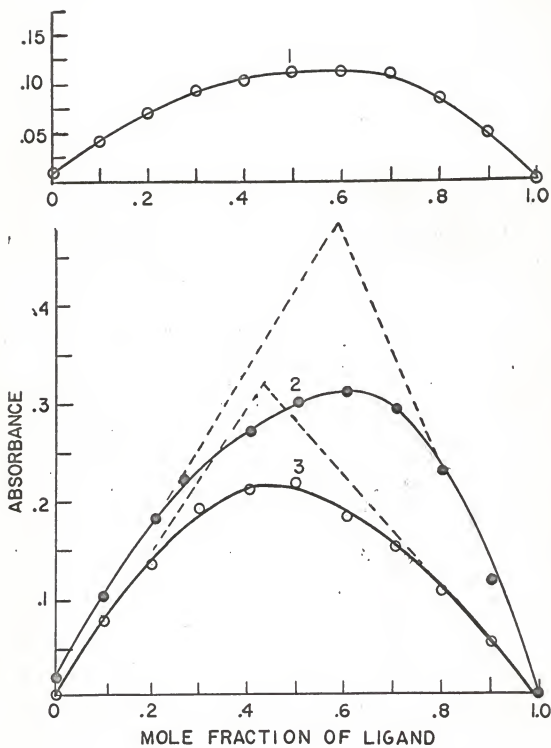
#### EXPLANATION OF FIGURE 16

Fig. 16. Continuous variations plots for cinnamohydroxamates of iron (III) and uranyl (II).

Plot 1 is for uranyl (II) cinnamohydroxamate at 380 m $\mu$  and pH 5.0.

Plot 2 is for uranyl (II) cinnamohydroxamate at 380 m $\mu$  and pH 4.0.

Plot 3 is for iron (III) cinnamohydroxamate at 510 m $\mu$  and pH 2.0.



Octanol (10 ml.) was pipeted into the beaker and the system was stirred for 5-10 minutes with a magnetic stirrer. The contents of the beakers were transferred to a separatory funnel where the alcohol and aqueous phases were separated. The organic layer was centrifuged for 10 minutes and its absorbance was read at 460 m $\mu$  using octanol as the blank solution.

The results of the ligand to metal ratio study are shown in Figure 17. Absorbance values increased almost in a linear fashion with reagent up to ratios of 8:1. After this, the slope of the curve tapers off rapidly until at ligand to metal ratios of 15:1, after which point increases in ligand to metal ratios will not bring about any increase in the absorbance of the complex.

This would imply that in any determination of vanadium with cinnamohydroxamic acid, the ligand to metal ratio should be at least 8:1 and that using ligand in excess of a 15:1 ratio would be needless. It should be pointed out that greater care must be taken in allowing the ligand and metal to reach equilibrium at ratios of 8:1 than those at 15:1. This is accomplished by stirring the solution for a longer period of time and keeping the stirring time constant for each concentration of vanadium.

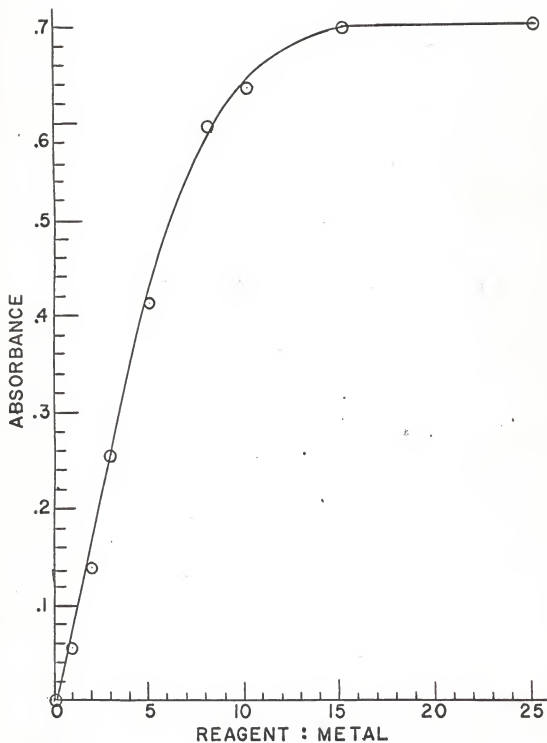
As vanadium (V) cinnamohydroxamate has such a high molar absorptivity, a procedure is listed below whereby vanadium (V) can be determined spectrophotometrically.

#### Procedure for Determination of Vanadium (V) with CHA

Pipet an aliquot of vanadium (V) solution containing 1.0 to 10.0

EXPLANATION OF FIGURE 17

Fig. 17. Effect of ligand to metal ratio on absorbance of vanadium (V) cinnamohydroxamate.



$\times 10^{-7}$  moles of vanadium into a 100 ml. beaker. Pipet CHA (10 ml. of 0.01 M) into the beaker and add distilled water so that the total volume is approximately 25 ml. Adjust the pH of the solution to 2.0 using a pH meter to measure the pH, and stir the solution for five to ten minutes with a magnetic stirrer. Remove the electrodes from the solution and wash them with distilled water adding the wash solution to the beaker containing the vanadium (V) cinnamohydroxamate. Octanol, (10 ml.) which has previously been distilled, saturated with water, and stored in a brown bottle is pipeted into the beaker. Stir the two-phase system for five minutes and transfer the contents to a 125 ml. separatory funnel. Shake the funnel several times and allow to stand until the organic and aqueous phases separate. Drain the aqueous phase through the stopcock and pour the octanol solution out through the top of the funnel. Centrifuge the extract for ten minutes to remove any remaining water from the organic extract and read the percent transmission of the extract on a spectrophotometer at a wavelength of 450 m $\mu$  using octanol as the blank. From a previously prepared calibration chart, the transmission reading taken is used to find the concentration of vanadium (V) in the original aliquot of vanadium solution.



## SUMMARY

Cinnamohydroxamic acid and potassium 2-furohydroxamate were prepared from their esters and alkaline solutions of hydroxylamine hydrochloride. Qualitative observations were made to ascertain which metal ions form colored complexes with nicotinohydroxamic acid, cinnamohydroxamic acid, and potassium 2-furohydroxamate. Nicotinohydroxamates of Ti (IV),  $\text{UO}_2$  (II), and Mo (VI) were selected for more intense study. Spectra were obtained, adherence to Beer's law was investigated, and continuous variations studies were made on the three chelates.

Similarly, furohydroxamates of Os (VIII), Fe (III), Ti (IV),  $\text{UO}_2$  (II), and V (V) were investigated in the same manner as the nicotinohydroxamates. In addition, it was found that 1-octanol would quantitatively extract vanadium (V) furohydroxamate.

Cinnamohydroxamates appeared to be less soluble in water but did possess a more intense color than the corresponding nicotinohydroxamate or furohydroxamate. Vanadium (V) cinnamohydroxamate and uranyl (II) cinnamohydroxamate were extracted quantitatively from aqueous solution with 1-octanol and the extracts followed Beer's law. Structure studies were made on the cinnamohydroxamates of Fe (III) and  $\text{UO}_2$  (II). The effect of ligand to metal ratio on color intensity was examined for V (V) cinnamohydroxamate. A procedure was suggested whereby vanadium could be determined spectrophotometrically using cinnamohydroxamic acid as an analytical reagent.

## ACKNOWLEDGEMENT

The author wishes to express his thanks to his major professor, Dr. C. E. Meloan, for the assistance and encouragement given by him during the course of this research.

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SPECTROPHOTOMETRIC STUDY ON  
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AND POTASSIUM 2-FUROHYDROXYAMATE

by

RONALD GENE ROWLAND

B. S., Kansas State University, 1959

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1965

Approved by:

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Major Professor

## ABSTRACT

Many articles are found in the literature describing hydroxamic acids as analytical reagents for determination of various transition metal ions--both gravimetrically and spectrophotometrically. In this investigation, it was desired to study spectrophotometrically the chelates of nicotinohydroxamic acid, cinnamohydroxamic acid, and potassium 2-furohydroxamate with available metal ions.

Spectra in the visible region were obtained for the nicotino-hydroxamates of Ti (IV), Mo (VI), and  $\text{UO}_2$  (II). Continuous variations studies showed a 1:4 metal to ligand complex for Ti (IV) at pH 8.0, a 1:2 complex for Mo (VI) at pH 3.0, a 1:2 complex for  $\text{UO}_2$  (II) at pH 7.0, and a mixture of 1:1 and 1:2 metal to ligand complexes for  $\text{UO}_2$  (II) at pH 3.0. All the nicotinohydroxamates studied except Mo (VI) followed Beer's law. This deviation was due to insufficient quantities of reagent to tie up all the metal at higher metal concentration values. Extraction attempts made on the three nicotinohydroxamates proved to be unsuccessful as none of the organic solvents tried would extract the chelates.

Spectra in the visible region were obtained for the furohydroxamates of  $\text{UO}_2$  (II), V (V), Os (VIII), Fe (III), and Ti (IV), at pH values where the chelates formed their most intensely colored complexes. Beer's law studies were made on all of the above complexes except Os (VIII) and the chelates followed Beer's law in the concentration ranges examined. Continuous variations studies showed a 1:1 complex to exist for Fe (III) at pH 2.0, a 4:1 complex for Ti (IV) at

pH 9.0, and a 2:1 metal to ligand complex for Os (VIII) at pH 6.0.

Polar, oxygenated solvents such as 1-octanol were found to be suitable for quantitatively extracting vanadium (V) cinnamohydroxamate and vanadium (V) furohydroxamate from aqueous solution.

Vanadium (V) furohydroxamate was extracted from aqueous solution of pH 3.0 with 1-octanol and the absorbance of the complex was measured at 450 m $\mu$ . The chelate had a molar absorptivity of  $2.6 \times 10^3$  in octanol.

Uranyl (II) cinnamohydroxamate was extracted from aqueous solution of pH 9.0 with 1-octanol and the absorbance was measured at 380 m $\mu$ . The chelate had a molar absorptivity of  $6.9 \times 10^3$ .

Vanadium (V) cinnamohydroxamate was extracted from aqueous solution of pH 2.0 with 1-octanol and the absorbance of the extract was read at 460 m $\mu$ . The vanadium complex had a molar absorptivity of  $7.0 \times 10^3$ .

Continuous variations studies on uranyl (II) cinnamohydroxamate at pH 4.0 and 5.0 showed an equilibrium mixture of 1:1 and 2:1 ligand to metal chelates to be present in aqueous solution. A similar study on iron (III) cinnamohydroxamate showed a 1:1 complex to be formed at pH 2.0.

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It was found that a ligand to metal ratio of 15 to 1 is necessary for maximum color formation in the case of vanadium (V) cinnamohydroxamate. A suggested procedure is given for the determination of vanadium spectrophotometrically with cinnamohydroxamic acid.